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<b>(21) International Application Number:</b> PCT/CA96/00116 <b>(22) International Filing Date:</b> 27 February 1996 (27.02.96) <b>(30) Priority Data:</b> 08/397,604 1 March 1995 (01.03.95) US <b>(71) Applicant:</b> ALCAN INTERNATIONAL LIMITED [CA/CA]; 1188 Sherbrooke Street West, Montreal, Quebec H3A 3G2 (CA). <b>(72) Inventors:</b> DAVISSON, Thomas, Lee; 1489 Radcliff Drive, Aurora, IL 60504 (US). REESOR, Douglas, Neil; 232 Highland Court, Terre Haute, IN 47802 (US). NADKARNI, Sadashiv, Kashinath; 85 Kendall Road, Lexington, MA 02173 (US). <b>(74) Agents:</b> GALE, Edwin, J. et al.; Kirby, Eades, Gale, Baker, Station D, P.O. Box 3432, Ottawa, Ontario K1P 6N9 (CA).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ALUMINUM ALLOY COMPOSITION AND METHODS OF MANUFACTURE		
<b>(57) Abstract</b>  The invention provides a new aluminum-based alloy having properties which mimic homogenized DC cast 3003 alloy, and a low-cost method for manufacturing the alloy. The alloy contains 0.40 % to 0.70 % Fe, 0.10 % to less than 0.30 % Mn, more than 0.10 % to 0.25 % Cu, less than 0.10 % Si, optionally up to 0.10 % Ti, and the balance Al and incidental impurities. The alloy achieves properties similar to homogenized DC cast 3003 alloy when continuously cast, followed by cold rolling and, if desired, annealing at final gauge. Surprisingly, no other heat treatments are required.		

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ALUMINUM ALLOY COMPOSITION AND METHODS OF MANUFACTURETECHNICAL FIELD

This invention relates to aluminum alloy sheet products and methods for making such products. More specifically, this invention relates to a new aluminum alloy which can be substituted for conventional homogenized DC cast 3003 alloy in any temper, as a rolled, partially annealed or fully annealed product, and a method of making such a product. An important preferred aspect of the present invention is a new aluminum alloy suitable for use in household foil and semi-rigid foil containers having a combination of strength and formability, and an economical method for the manufacture of the alloy using a continuous caster.

BACKGROUND ART

Semi-rigid foil containers are manufactured from aluminum sheet rolled to a thickness of 0.005 - 0.025 cm (0.002 - 0.010 inches). The sheet is then cut to a desired shape and formed into self supporting containers commonly used for food items such as cakes, pastries, entrees, cooked vegetables, etc. Generally the term "sheet" will be used herein to refer to as cast or rolled alloy having a thickness that is relatively thin compared to its width and includes the products commonly referred to as sheet, plate and foil.

Conventional 3003 aluminum alloy is commonly used for this application. The conventional method for manufacturing 3003 alloy is to direct chill (DC) cast an ingot of manganese-containing aluminum alloy, homogenize the ingot by heating to a temperature sufficient to cause most of the manganese to go into solid solution, cool and hold at a temperature where a significant portion of the manganese precipitates out of solution, hot roll the ingot to a predetermined intermediate gauge, cold roll to final gauge, optionally with interannealing between at least some of the cold rolling

passes, and then annealing the cold rolled alloy sheet to the desired temper. Typical mechanical properties of 3003 alloy produced in this manner is shown in Table 1 below:

5

**TABLE 1**

Typical Mechanical Properties of 3003 Alloy

10

Temper	UTS(Ksi)	YS(Ksi)	Elong.%	Olsen
As Rolled	34.8	30.8	2	-
H26	24.6	23.3	11	0.208
H25	23.1	20.5	15	0.248
H23	22.2	18.5	18	0.251
O	15.1	7.0	20	0.268

Furthermore, DC cast 3003 alloy is relatively insensitive to variations in the final annealing process allowing for reproducible properties that are consistent from coil to coil. For example, variations in the properties of DC cast 3003 alloy annealed at various temperatures are shown in Table 2 below:

20

**TABLE 2**

Properties of DC Cast 3003

25

Annealing Temp °C	UTS (Ksi)	YS (Ksi)	Elongation %
As rolled	42.2	37.5	2.0
250	27.2	24.5	2.2
260	24.7	21.5	10.4
270	23.8	20.2	13.8
280	22.6	17.8	16.4
290	21.6	14.0	-
350	16.4	7.5	22.4

Because of these useful properties DC cast 3003 alloy has found numerous uses and DC cast 3003 alloy is a commonly used alloy. A typical composition for 3003 alloy, including maximum and minimum limits, is as shown  
5 below:

	Cu:	0.14 (0.05 - 0.20) %
	Fe:	0.61 ((0.7 max.) %
	Mn:	1.08 (1.0 - 1.5) %
	Si:	0.22 (0.6 max.) %
10	Zn:	0.00 (0.10 max.) %
	Ti:	0.00 (0.10 max.) %
	Balance:	Al and incidental impurities.

This alloy belongs to the category of dispersion-hardened alloys. With aluminum alloys, dispersion  
15 hardening may be achieved by the addition of alloying elements that combine chemically with the aluminum, or with each other, to form fine particles that precipitate from the matrix. These fine particles are uniformly distributed throughout the crystal lattice in such a way  
20 as to impede the movement of dislocations causing a hardening effect. Manganese is such an alloying element. Manganese is soluble in liquid aluminum but has a very low solubility in solid aluminum. Therefore, as 3003 alloy cools down after casting, dispersoids form  
25 at the expense of Mn in solution. The dispersoids are fine particles of  $MnAl_6$  and alphas-manganese ( $Al_{12}Mn_3Si_2$ ).

The formation of these dispersoids is a slow process, and in practice more than 60% of the Mn remains in solution after DC cast 3003 ingots have solidified. During homogenization, the dispersoids tend to go into solid solution until equilibrium is reached. During subsequent slow cooling, dispersoids form from about 80% of the available Mn.

Continuous casting, on the other hand, can produce products having substantially different properties from those of dispersion-hardened alloys, because cooling rates are generally much faster than with DC casting. Continuous casting can also be more productive than DC casting, because it permits the casting of shapes that are closer to common sheet dimensions, requiring less rolling to produce the final gauge. Several continuous casting processes and machines have been developed or are in commercial use today for casting aluminum alloys specifically for rolling into sheet. These include twin belt casters, twin roll casters, block casters, single roll casters and others. These casters are generally capable of casting a continuous sheet of aluminum alloy less than 5 cm (2 inches) thick and as wide as the design width of the caster. Optionally, the continuously cast alloy can be rolled to a thinner gauge immediately after casting in a continuous hot rolling process. The sheet may then be coiled for easy storage and transportation. Subsequently, the sheet may be hot-

or cold-rolled to the final gauge, optionally with one or more interannealing or other heat treatment steps.

DISCLOSURE OF THE INVENTION

The present invention relates to a new aluminum alloy and a simple method for its manufacture. Stated broadly, the alloy contains more than 0.10% and up to 0.25% by weight of copper, at least 0.10% and less than 0.30% by weight of manganese, at least 0.40% and up to 0.70% of iron, less than 0.10% by weight of silicon and optionally up to 0.10% of titanium (as a grain refiner), with the balance being aluminum and incidental impurities.

This alloy can be continuously cast to form a product having properties very similar to homogenized DC cast 3003. The process involves continuous casting (optionally with continuous hot rolling immediately after casting), cooling the cast sheet, cold rolling to final gauge and finally, if desired, partially or fully annealing. This process does not require any intermediate heat treatments such as homogenization, solution heat treatments or interannealing. Accordingly, the process of the present invention is simpler and more productive compared to most conventional aluminum sheet production processes which generally do involve at least some form of intermediate heat treatments, such as the DC casting route conventionally used to produce 3003 alloy.

BEST MODES FOR CARRYING OUT THE INVENTION

When a conventional 3003 alloy composition was cast on a continuous caster without homogenization, most of the Mn remained in solid solution. The presence of  
5 higher amounts of Mn in solid solution and lower amounts of dispersoids has the effect of making the alloy stronger and lower in formability. The higher amount of Mn in solid solution is believed to retard the process of recrystallization while at the same time increasing  
10 the strength of the alloy by solid-solution hardening. The dispersoids act as pins during rolling, preventing the grains from growing too large due to recrystallization. Smaller grain sizes are generally associated with better formability.

15 It has now been found that an alloy having properties similar to DC cast, homogenized 3003 alloy can be produced by continuous casting the alloy of the present invention and processing it to final gauge without the need for any intermediate heat treatments.  
20 The properties achieved are sufficiently similar to DC cast homogenized 3003 that the present alloy can be directly substituted in current commercial applications for 3003 alloy without having to change the processing parameters, or having any noticeable effect on the  
25 product produced.

The present alloy contains copper in an amount in excess of 0.10% and up to 0.25% by weight and preferably between 0.15% and 0.25%. Copper contributes to the



strength of the alloy and must be present in an amount adequate to provide the necessary strengthening. Also, within these limits, some beneficial effect on elongation at a given annealing temperature has been  
5 observed that is attributable to copper. This provides the desirable degree of formability in the final product. Excessive copper will make the alloy undesirable for mixing with used beverage can scrap to be recycled into 3004-type alloy. This would decrease  
10 the value of the alloy for recycling.

The alloy of the present invention contains at least about 0.10% manganese but less than 0.30%. Preferably, the manganese level is between about 0.10% and 0.20% by weight. The manganese level is optimally  
15 the minimum level that is just adequate to provide the necessary solid solution hardening, and no more, and will therefore not precipitate during subsequent operations. If the manganese level is increased above the described levels, part of the manganese will form  
20 dispersoids during processing in a manner that is sensitive to the exact processing conditions and can result in properties that change rapidly and less predictably during annealing, making it harder to reproduce properties from coil to coil.

25 The iron level in the alloy of the present invention should be maintained between about 0.40% and about 0.70% and is preferably maintained above 0.50% and most preferably above 0.60% by weight. The iron

initially reacts with the aluminum to form  $\text{FeAl}_3$  particles which act as pins retarding grain growth during processing. These particles effectively substitute for the  $\text{MnAl}_6$  particles present in homogenized DC cast 3003 alloy. As very little iron exists in solid solution, the problems associated with manganese do not exist. Generally, higher levels of iron are better in the present alloy; however, this must be balanced with the impact that iron levels can have on recycling. Like high copper alloys, high iron alloys are not as valuable for recycling because they cannot be recycled into valuable low iron alloys without blending in primary low iron metal to reduce the overall iron level in the recycled metal. In particular, beverage can sheet is currently one of the most valuable uses for recycled aluminum alloys, and it requires a low iron content. The alloy of the present invention contains less than 0.10% by weight silicon and preferably less than 0.07% Si. Silicon is a naturally occurring impurity in unalloyed aluminum, and may exceed 0.10% in some unalloyed aluminum. Accordingly, it may be necessary to select high purity primary aluminum for use in the present alloy. Silicon must be maintained at this low level to avoid reactions with the  $\text{FeAl}_3$  particles. This reaction tends to take place during cooling or any annealing process and can result in slower recrystallization and consequently larger grain sizes and lower elongation.  $\text{FeAl}_3$  particles are desirable in

the present alloy because they act as pins impeding grain growth. Titanium may optionally be present in an amount of up to 0.10% as a grain refiner.

The balance of the alloy is aluminum with  
5 incidental impurities. It should be noted that even though iron and silicon are normal incidental impurities in unalloyed aluminum, they generally do not occur in the ratios required for the present alloy. If silicon is low enough, the iron will tend to be too low, and if  
10 iron is within the desired range, the silicon will generally be too high. Accordingly, in preparing the present alloy it is generally necessary to select an unalloyed aluminum with relatively low levels of impurities, and add additional iron before casting to  
15 provide the desired iron level in the alloy.

Primary metal is particularly useful for these purposes, and typically has the following specifications (before the addition of the necessary alloying elements):

20	Fe	<	0.7%
	Si	<	0.1%
	V	<	0.02%
	Ti	<	0.05%

Further selection of a low Si primary metal  
25 therefore provides a suitable starting material for the preferred composition of this alloy. After the alloy

has been melted and the composition adjusted within the above described limits, the alloy of the present invention is cast on a continuous casting machine adapted for making sheet products. This form of casting produces an endless sheet of relatively wide, relatively thin alloy. The sheet is desirably at least 61 cm (24 inches) wide and may be as wide 203 cm (80 inches) or more. In practice, the width of the casting machine generally determines the width of the cast sheet. The sheet is also generally less than 5 cm (2 inches) thick and is preferable less than 2.5 cm (1 inch) thick. It is advantageous that the sheet be thin enough to be coiled immediately after casting or, if the casting machine is so equipped, after a continuous hot rolling step.

The alloy of the present invention is usually then coiled and cooled to room temperature. After cooling the alloy is cold rolled to final gauge. Cold rolling is conducted in one or more passes. One advantage of the alloy of the present invention is that no heat treatments of any kind are required between casting and rolling to final gauge. This saves time and expense and requires less capital investment to produce the alloy. Homogenization is not required. Solution heat treatment is not required. Interannealing between passes during cold rolling is not required. Indeed, these heat

treatments have been found to alter the properties of the final alloy such that it no longer mimics the properties of homogenized DC cast 3003 alloy. Alloy products of the present invention produced in this fashion achieve an average grain size in the final gauge "O" temper of less than  $70 \times 10^{-6}$  m (70 microns) and preferably less than  $50 \times 10^{-6}$  m (50 microns), measured at the surface of the alloy. The "O" temper (fully annealed) is one of the tempers (along with fully hard H19 and partial annealed H2X) generally used for household foil and semi-rigid container applications.

The invention is described in more detail in the following with reference to the accompanying Examples. The Examples are not intended to limit the scope and generality of the invention.

#### EXAMPLES

Five alloys were cast on a twin belt continuous casting machine. The alloys contained the elements listed in Table 3 with the balance being aluminum and incidental impurities. The caster used was substantially as described in US Patent 4,008,750. The as-cast sheet had a thickness of about 1.6 cm (0.625 inches) and was immediately continuously hot rolled to a thickness of about 0.15 cm (0.06 inches).

Table 3

Composition of Continuously Cast Alloys

	Alloy	Cu%	Fe%	Mn%	Si%
5	A	0.20	0.65	0.42	0.06
	B	0.20	0.65	0.33	0.06
	C	0.15	0.65	0.20	0.06
	D	0.20	0.65	0.15	0.04
	E	0.20	0.45	0.15	0.06

10           The cast sheet was then coiled and allowed to cool to room temperature. After cooling the coiled sheets were conventionally cold rolled to a final gauge of 0.008 cm (0.003 inches) without interannealing.

Sections of the cold rolled sheets were annealed in  
15 the laboratory at various temperatures. Annealing was conducted by heating the samples at a rate of 50°C per hour and then holding the sample at the annealing temperature for 4 hours. The properties of the as-rolled sheet, the various partially annealed sheets and fully  
20 annealed ("O" temper) sheet were measured and are presented together with typical properties of DC cast 3003 alloy previously obtained using the same test methods and equipment. The "O" temper was produced by annealing at 350°C - 400°C for 4 hours. These measured  
25 properties are shown in Tables 4 - 7 below.

Alloy C was also prepared using an interanneal step. This involved cold rolling the strip to an intermediate thickness, annealing at 425°C for two hours then cold rolling to final gauge. This is  
30 designated as C(int) in Tables 4 to 6.

**TABLE 4**  
Yield Strength (Ksi)

Temp °C	A	B	C	C (int)	D	E	3003
5	As rolled	40.7	38.1	37.2	-	36.7	37.5
	245	30.1	29.6	26.6	20.6	25.7	-
	250	-	-	-	-	-	24.5
	260	28.9	27.7	23.8	19.6	24.4	21.5
	270	-	-	-	-	-	20.2
10	275	27.0	25.8	21.7	12.5	19.7	-
	280	-	-	-	-	-	17.8
	290	25.5	24.4	20.0	6.0	13.6	14.0
	305	22.2	18.7	-	-	9.3	-
15	"O" Temper	8.0	7.7	7.7	-	6.9	7.5

**TABLE 5**  
Elongation %

Temp °C	A	B	C	C (int)	D	E	3003
20	As Rolled	1.8	2.0	2.5	-	3.0	2.0
	245	2.2	2.2	4.0	3.0	5.0	-
	250	-	-	-	-	-	2.2
	260	2.3	2.7	5.0	3.0	9.5	10.4
	270	-	-	-	-	-	13.8
25	275	3.3	3.2	7.5	2.5	16.5	10.5
	280	-	-	-	-	-	16.4
	290	6.4	6.3	11.5	7.0	16.5	9.5
	305	6.2	5.8	-	-	22.0	18.0
30	"O" Temper	14.0	14.0	18.5	-	22.0	21.0

**TABLE 6**  
Olsen Values

Temp °C	A	B	C	C (int)	D	E	3003
35	245	0.157	0.146	0.206	0.110	0.188	0.145
	260	0.176	0.179	0.197	0.100	0.194	0.159
	275	0.180	0.181	0.216	0.100	0.216	0.185
	280	-	-	-	-	-	-
	290	0.184	0.193	0.215	0.200	0.200	0.158
	305	0.118	0.106	-	-	0.245	0.225
40	"O" Temper	low	low	0.230	-	0.257	0.237

**TABLE 7**  
Grain Size of "O" Temper Alloy

	A	B	C	D	E	3003
Grain Size in m x 10 <sup>-6</sup> (microns)	92-100	76-90	42-50	38	38-45	38

Yield strength and elongation were determined according to ASTM test method E8. Olsen values are a measure of formability and were determined by using a Detroit Testing machine with a 2.2 cm (7/8 inch) ball without applying any surface treatments, texturants or lubricants. Grain size was measured on the surface of the samples. If a range of values is shown, the range represents grain size measurements at various surface locations.

Samples A and B contain excess manganese and as shown in Table 7 developed large grains relative to the other samples and relative to the 3003 standard. As a result these samples exhibited low Olsen Values and low elongation indicating poor formability. Sample D is almost identical to DC cast 3003 in every respect. Sample E is similar and very good, however, the variation in Olsen Values with annealing temperature indicates that it may be somewhat harder to control the properties of this composition. Also, the somewhat lower Olsen Values indicate that the formability is not quite as good as sample D or the 3003 standard. This was confirmed during formability trials in which sample



D performed as well as DC cast 3003 and sample E performed well with most shapes, but was unacceptable for forming the most demanding shapes. Sample C is also very similar to the DC cast 3003. However, the grain size is a little higher and the Olsen values a little lower, indicate that the formability is a little lower. Sample C (int) has strength and formability properties that fell below the other samples tested, indicating that the preferred processing route using no interanneal does provide better properties.

In summary, the present invention teaches a new aluminum-based alloy composition and low cost method of manufacturing. The alloy of the present exhibits properties in all tempers similar to homogenized DC cast 3003 alloy and can be a suitable commercial substitute therefor in most applications.

Claims:

1. An aluminum-based alloy characterized in that the alloy contains, by weight, at least 0.4 and up to 0.7% iron, at least 0.1% and less than 0.3% manganese, more  
5 than 0.1% and up to 0.25% copper, less than 0.1% silicon, optionally up to 0.1% titanium, the balance being aluminum and incidental impurities.
2. An alloy according to claim 1 characterized in that the alloy contains titanium in an amount up to 0.1% by  
10 weight.
3. An alloy according to claim 1 characterized in that the alloy contains silicon in an amount of less than 0.07%.
4. An alloy according to claim 1 characterized in that  
15 the alloy contains iron in an amount of at least about 0.5%.
5. An alloy according to claim 1 characterized in that the alloy contains copper in an amount of at least about 0.15%.
- 20 6. An alloy according to claim 3 characterized in that the alloy contains iron in an amount of at least about 0.5%.

7. An alloy according to claim 3 characterized in that the alloy contains copper in an amount of at least about 0.15%.
8. An alloy according to claim 6 characterized in that the alloy contains copper in an amount of at least about 0.15%.
9. An alloy according to claim 8 characterized in that the alloy contains titanium in an amount of up to 0.1%.
10. An alloy according to claim 1 characterized in that the alloy has an average grain size of less than about  $70 \times 10^{-6}$  m (70 microns) when annealed to an "O" temper.
11. A method of manufacturing a sheet of aluminum-based alloy comprising continuously casting an aluminum-based alloy, cooling the alloy, cold rolling the alloy to form a sheet of aluminum based alloy having a desired final gauge, and optionally annealing the sheet of aluminum based alloy after said cold rolling is complete; characterized in that the aluminum-based alloy comprising by weight at least 0.4% up to 0.7% iron, at least 0.1% and less than 0.3% manganese, more than 0.1% and up to 0.25% copper, less than 0.1% silicon, and optionally up to 0.1% titanium, the balance being aluminum and incidental impurities.

12. A method according to claim 11 characterized in that the alloy is subjected to homogenization after casting.

13. A method according to claim 11 characterized in  
5 that the sheet of aluminum-based has an average grain size of less than about  $70 \times 10^{-6}$  m (70 microns) when annealed to an "O" temper.

14. A method according to claim 11 characterized in that the cold rolling is conducted in more than one  
10 pass.

15. A method according to claim 14 characterized in that the sheet of aluminum-based alloy is not interannealed between said passes.

16. A method according to claim 11 characterized in  
15 that the alloy is not subjected to any heat treatments after casting and before cold rolling to final gauge.

17. A method according to claim 16 characterized in that the alloy has a grain size of less than about  $70 \times 10^{-6}$  m (70 microns) when annealed to an "O" temper.

# INTERNATIONAL SEARCH REPORT

International Application No.

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A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C22C21/00 C22F1/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C22C C22F

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,91 14794 (ALCAN INTERNATIONAL LIMITED) 3 October 1991 see claims 1-10	1
A	EP,A,0 289 844 (VEREINIGTE ALUMINIUMWERKE AKTIENGESELLSCHAFT) 9 November 1988	1
A	JP,A,60 251 246 (KOBÉ SEIKOSHO K.K.) 11 December 1985	1
A	JP,A,00 038 501 (FURUKAWA ALUMINUM CO. LTD. JAPAN) 16 January 1991 see table 1	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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